Palladium-Catalyzed Arylation of the THP Derivative of (*Z*)-2-Butene-1,4-diol with Arenediazonium Salts and the Synthesis of β-Aryl-γ-butyrolactones

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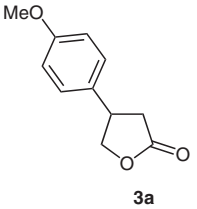
Abstract: The reaction of arenediazonium tetrafluoroborates with the THP derivative of (*Z*)-2-butene-1,4-diol in the presence of $Pd(OAc)_2$ in MeOH at 35 °C gives 4-aryl-2-methoxytetrahydrofurans in good to high yields. The reaction tolerates a variety of useful functional groups including ester, keto, cyano, nitro, chloro, and bromo functionalities as well as *ortho* substituents. Based on this process, γ-aryl-β-butyrolactone derivatives can be prepared via a sequential palladium-catalyzed arylation–cyclization–oxidation protocol that omits the isolation of 4-aryl-2-methoxytetrahydrofuran intermediates.

Key words: arenediazonium salts, palladium, Mizoroki–Heck reaction, tetrahydrofurans, allylic alcohols

After the first palladium-catalyzed arylation of olefins with arenediazonium salts reported by Matsuda et al.,[1] arenediazonium salts have been used as aryl partners in a large number of Mizoroki–Heck reactions,[2] including the palladium-catalyzed arylation of allylic alcohols to afford saturated carbonyl compounds.[1,3] The reaction of arenediazonium salts with 2-butene-1,4-diol, however, has not been investigated.[4] The related reaction with aryl iodides or vinyl halides and triflates gives substituted 2-hydroxytetrahydrofurans **1**[5,6] (Scheme 1), which have been used as precursors of butyrolactone derivatives. Extending this type of Mizoroki–Heck–cyclization process to arenediazonium salts would be a convenient route to tethering an oxygen-containing five-membered ring to aniline precursors. Therefore, as part of a program devoted to the utilization of arenediazonium salts in palladium-catalyzed reactions,[6,7] we became interested in investigating whether a reactivity similar to that observed with aryl iodides or vinyl halides and triflates might be observed using arenediazonium tetrafluoroborates. Herein we report the results of this study.

We started our study by examining the reaction of commercially available (*Z*)-2-butene-1,4-diol with 4-methoxydiazobenzene tetrafluoroborate (**2a**) and 4-methoxycarbonyldiazobenzene tetrafluoroborate (**2b**), models of electron-rich and electron-poor arenediazonium salts, respectively. Reactions were performed in the presence of 5 mol% of $Pd(OAc)_2$. Disappointing results were obtained with **2a** under a number of conditions varying the **2a** to (*Z*)-2-butene-1,4-diol molar ratios, using THF, MeCN, and MeOH as solvents at temperatures ranging from room temperature to 60 °C. Complex reaction mixtures were usually formed that we have not carefully analyzed. No evidence of 2-hydroxytetrahydrofuran formation (**1a**, R = 4-$MeOC_6H_4$) was attained. In some cases, variable amounts of 1,4-dimethoxybenzene and butyrolactone **3a** (formed via trapping the arenediazonium salt with MeOH and an oxidation process, respectively, Figure 1) were isolated.

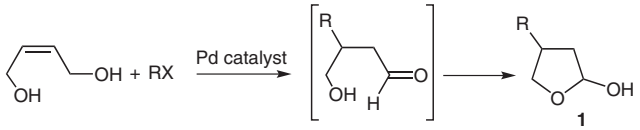


3a

Figure 1

A similar behavior was observed when **2b** was subjected to the same arylation–cyclization conditions in THF and MeCN. Interestingly, treatment of 1 equivalent of **2b** with 2 equivalents of (*Z*)-2-butene-1,4-diol and 5 mol% of $Pd(OAc)_2$ in MeOH for 5 hours at 35 °C led to the isolation of the 2-methoxytetrahydrofuran derivative **5b** as an approximately *trans*/*cis* (60:40) diastereomeric mixture[8] in 26% yield (Scheme 2). Very likely, **5b** is generated via trapping of the carbocationic intermediate **4b** by MeOH.[9] The formation of **4b** from the corresponding 2-hydroxytetrahydrofuran is in turn favored by the acidity of the reaction medium, the increase of which parallels the proceeding of the vinylic substitution [regeneration of Pd(0) from HPd, which is generated in the *syn*-β-elimination step, leads to the formation of fluoroboric acid].

As 2-methoxytetrahydrofurans can be useful synthetic intermediates (e.g., acetals of this type can be converted into the corresponding lactones via oxidation[10]), we decided to investigate this reaction more in detail. However, the 2-methoxytetrahydrofuran **5b** was isolated only in moderate yields under a variety of conditions. The best result (54% yield) was obtained when 2 equivalents of **2b** were treated



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Scheme 1

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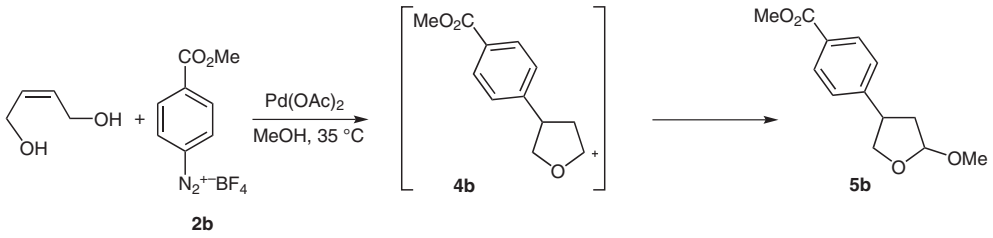


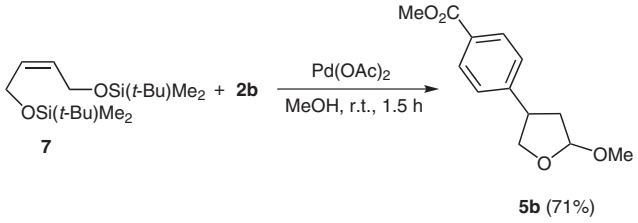
Scheme 2

with 1 equivalent of (*Z*)-2-butene-1,4-diol and 5 mol% of $Pd(OAc)_2$ in MeOH at 35 °C for 45 minutes.

It is unclear as to exactly what is the reason of the complex reaction mixtures obtained with **2a** and the moderate yield obtained with **2b**. In general, arenediazonium salts are not as stable as other aryl donors such as aryl halides or triflates, and their successful utilization in palladium-catalyzed reactions depends on a subtle balance between their stability and the rate of their involvement in catalytic cycles. In this case, in the presence of the free hydroxy groups, it is possible that the vinylic substitution reaction is relatively slow in comparison to their stability under reaction conditions and that a number of side reactions can take place. Therefore, we switched to the utilization of the THP derivative **6** as the starting olefin. The working hypothesis was that converting the alcoholic groups into their THP derivatives might allow for a cleaner and more efficient vinylic substitution and that the acidic medium resulting from the vinylic substitution might have its effect on the acid-labile protecting groups (i.e., regenerating the free alcoholic groups) at an advanced stage of the reaction, if not after completion of the vinylic substitution step. Once the free alcoholic groups are regenerated, the arylated intermediates should afford the desired 2-methoxytetrahydrofurans.

After some experimentations, we were pleased to find that **5a** could be isolated in 72% yield upon treatment of 2 equivalents of **2a** with 1 equivalent of **6** and 5 mol% of $Pd(OAc)_2$ in MeOH at 35 °C for 1 hour (Table 1, entry 3). The screening was then extended to **2b** (Table 1, entries 4–8) and showed that the same conditions could be successfully used even with an electron-poor arenediazonium salt (Table 1, entry 8).

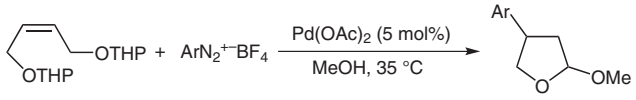
The utilization of a silyl protecting group was also briefly investigated by treating **2b** with **7** (Scheme 3). Although **5b** was isolated in high yield, the THP derivative appears to be superior.



Scheme 3

Using the optimized conditions, the reaction was then extended to include other arenediazonium salts.[11] As shown in Table 2, the desired products were isolated in good to high yields and a variety of useful functional groups, including ester, keto, cyano, nitro, chloro, and bromo functionalities, are tolerated making this method particularly appealing for subsequent synthetic manipulations, for example, with halogen-containing derivatives (Table 2, entries 11, 12, and 16), via cross-coupling reactions. Arenediazonium salts bearing *ortho* substituents can also be successfully used (Table 1, entries 8, 12, 13, 15, 16). The low yield observed with 4-iododiazobenzene tetra-

Table 1 Optimization of the Reaction Conditions[a]



Entry	**2** (equiv)		THP derivative **3** (equiv)	Time (h)	Yield (%) of **5**[b]	
1	**2a**	(1)	1	2	**5a**	29
2	Ar = 4-$MeOC_6H_4$	(1.5)	1	1	**5a**	62
3		(2)	1	1	**5a**	72
4	**2b**	(1)	1	3	**5b**	40
5	Ar = 4-$MeO_2CC_6H_4$	(1)	2	0.75	**5b**	67
6		(1)	2	1	**5b**	70
7		(1.2)	1	1	**5b**	73
8		(2)	1	0.75	**5b**	83

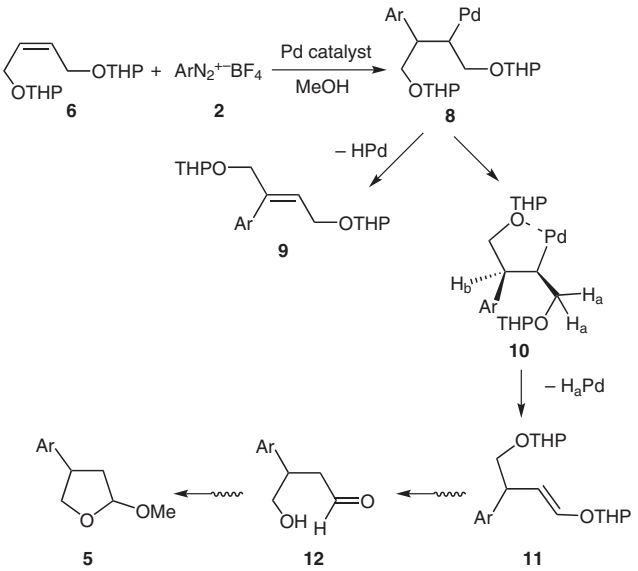
[a] Reactions were carried out on a 0.5 mmol scale in 4 mL of anhyd MeOH.
[b] Yields are given for isolated products.

Table 2 Palladium-Catalyzed Reaction of Arenediazonium Salts **2** with the THP derivative of (*Z*)-2-Butene-1,4-diol **6**[a]

Entry	Ar of **2**	Time (min)	Yield (%) of **5**[b,c]	
1	4-$MeOC_6H_4$	60	**5a**	72
2	4-$MeO_2CC_6H_4$	45	**5b**	83
3	3-$F_3CC_6H_4$	80	**5c**	67
4	4-NCC_6H_4	90	**5d**	74
5	4-$O_2NC_6H_4$	30	**5e**	72
6	4-$MeCOC_6H_4$	30	**5f**	72
7	4-MeC_6H_4	30	**5g**	89
8	2,4-$Me_2C_6H_3$	45	**5h**	68
9	4-FC_6H_4	30	**5i**	72
10	Ph	30	**5j**	76
11	4-ClC_6H_4	40	**5k**	76
12	2-ClC_6H_4	30	**5l**	64
13	2-Me-4-FC_6H_3	45	**5m**	90[d]
14	4-IC_6H_4	60	**5n**	34
15	2-$MeOC_6H_4$	30	**5o**	76
16	2-BrC_6H_4	40	**5p**	77

[a] Reactions were carried out on a 0.5 mmol scale using **2** (2 equiv), **6** (1 equiv), $Pd(OAc)_2$ (5 mol%) in MeOH (4 mL) at 35 °C.
[b] Yields are given for isolated products.
[c] Compounds **2** were isolated as approximately 60:40 *trans*/*cis* diastereomeric mixtures.
[d] Calculated by GC analysis.

fluoroborate (Table 2, entry 14) is most probably due to the competing oxidative addition of the C–I bond (in the starting arenediazonium salt and/or in the final product) to Pd(0) species. The resulting arylpalladium intermediates



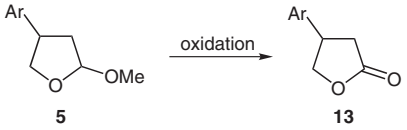
Scheme 4

can undergo several side reactions that we have not investigated.

Most probably, the success of the reaction is due inter alia to the high regioselectivity of the elimination step. As shown in Scheme 4, where a possible rationale for this reaction is outlined, the carbopalladation adduct **8** is likely to undergo a selective elimination of HPd, possibly via the cyclic intermediate **10** generated via oxygen coordination to palladium. Indeed, as only the hydrogens H_a can fit the steric requirements needed for the *syn*-β-elimination of HPd species, its formation can direct the elimination step so as to give selectively the enol ether **11**. No evidence was attained of **9** or compounds derived from its decomposition. The desired product **5** is subsequently formed from **11** through the intermediacy of the aldol **12**.

We next turned our attention to the conversion of 2-methoxytetrahydrofurans **5** into the corresponding γ-butyrolactones **13**. The results of our screening with the

Table 3 Oxidation of **5a** and **5b**[a]

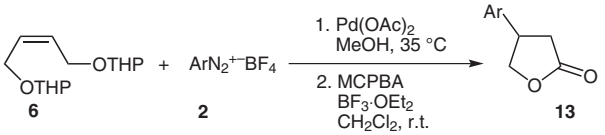


Entry	Ar	Oxidation system, solvent	Time (h)	Yield (%) of **13**[b]	
1	4-$MeOC_6H_4$	MCPBA, $BF_3{\cdot}OEt_2$, CH_2Cl_2	12	**13a**	80
2	4-$MeO_2CC_6H_4$	MCPBA, $BF_3{\cdot}OEt_2$, CH_2Cl_2	16	**13b**	88
3		CrO_3, H_2SO_4–Me_2CO–H_2O	24	**13b**	70[c]
4		Jones reagent (0.2 M)–Me_2CO	21	**13b**	73
5		Oxone–1,4-dioxane	24	**13b**	38[d]

[a] Unless otherwise stated, reactions were carried out on a 0.5 mmol scale at r.t. using: a) MCPBA (1 equiv), $BF_3{\cdot}OEt_2$ (0.4 equiv) in CH_2Cl_2 (3 mL); b) CrO_3 (1.5 equiv), H_2SO_4 (0.3 equiv) in Me_2CO–H_2O (8 mL; 75:25); c) Jones reagent (1.5 equiv, 0.2 M) in Me_2CO (5 mL); d) Oxone (3 equiv) in 1,4-dioxane (5 mL).
[b] Yields are given for isolated products.
[c] The starting material was recovered in 18% yield.
[d] At 80 °C.

oxidation systems that we have investigated are shown in Table 2. Best results were obtained using MCPBA and $BF_3{\cdot}OEt_2$[10a] in CH_2Cl_2 at room temperature (Table 3, entries 1 and 2).

Table 4 Preparation of β-Aryl-γ-butyrolactones **13** Omitting the Isolation of 4-Aryl-2-methoxytetrahydrofuran Intermediates **5**[a]



Entry	Ar of **2**	Yield (%) of **13**	
1	4-$MeOC_6H_4$	**13a**	50
2	Ph	**13j**	69
3	4-$MeO_2CC_6H_4$	**13b**	74

[a] Reactions were carried out on a 0.5 mmol scale using: (step 1) **2** (2 equiv), **6** (1 equiv), $Pd(OAc)_2$ (5 mol%) in MeOH (4 mL) at 35 °C; (step 2) MCPBA (1 equiv), $BF_3{\cdot}OEt_2$ (0.4 equiv) in CH_2Cl_2 (3 mL) at r.t.

To make this overall approach to β-aryl-γ-butyrolactones more attractive from a synthetic standpoint, the whole process (palladium-catalyzed arylation–cyclization–oxidation) was conducted so as to avoid the isolation of 2-methoxytetrahydrofuran intermediates.[12] In practice, oxidations were carried out on the crude reaction mixtures after extraction and filtration through a short bed of silica gel. The results obtained are listed in Table 4.

In conclusion, we have shown that arenediazonium tetrafluoroborates can be efficiently used as aryl donors in the palladium-catalyzed arylation–cyclization of the THP derivative of (*Z*)-2-butene-1,4-diol to give 4-aryl-2-methoxytetrahydrofurans usually in good to high yields. The reaction occurs under mild conditions and tolerates a variety of useful functional groups including ester, keto, cyano, nitro, chloro, and bromo functionalities as well as *ortho* substituents. Based on this process, β-aryl-γ-butyrolactone derivatives can be prepared via a sequential palladium-catalyzed arylation–cyclization–oxidation protocol that omits the isolation of 4-aryl-2-methoxytetrahydrofuran intermediates. Further studies on this chemistry are currently under way.

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(8) The stereochemistry of **5b** was assigned by NMR analysis. That of the other 4-aryl-2-methoxytetrahydrofuran derivatives has been assigned based on these data.
(9) Alternatively, as suggested by one of the referees, **5b** might arise from **4b** via proton loss and addition of MeOH to the resultant dihydrofuran (although no evidence was attained of the formation of such an intermediate). The tendency of furanols **1** to dehydrate upon distillation has been described: (a) Chalk, A. L.; Magennis, S. A. *J. Org. Chem.* **1976**, *41*, 273. In the case of formation of the dihydrofuran intermediate, the addition of MeOH to the carbon–carbon

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(11) **Preparation of 4-Aryl-2-methoxytetrahydrofuran (5) via Palladium-Catalyzed Reaction of Arenediazonium Tetrafluoroborates 2 with the THP Derivative of (*Z*)-2-Buten-1,4-diol (6) – Typical Procedure**

To a stirred solution of **6** (128.2 mg, 0.50 mmol) and $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) in anhyd MeOH (4.0 mL), **2a** (221.9 mg, 1.0 mmol) was added at r.t. under argon. The reaction mixture was warmed at 35 °C and stirred for 1 h (the reactor was protected from light with aluminium film). After cooling, the reaction mixture was diluted with Et_2O, washed with a sat. $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel [*n*-hexane–EtOAc, 75:25 (v/v)] to afford 75.2 mg (72% yield) of **5a** as an approximately 60:40 diastereomeric mixture. The *cis*-isomer was isolated and characterized.

Oil. IR (neat): 2940, 1606, 1077 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 5.19–5.15 (dd, J_1 = 5.5 Hz, J_2 = 3.0 Hz, 1 H), 4.17 (t, *J* = 8.0 Hz, 1 H), 3.81 (s, 3 H), 3.76–3.71 (m, 1 H), 3.45 (s, 3 H), 3.39–3.32 (m, 1 H), 2.70–2.52 (m, 1 H), 2.00–1.85 (m, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.4, 133.2, 128.7, 114.0, 110.8, 105.9, 73.2, 55.3, 55.0, 43.6, 41.2. MS: *m/z* (%) = 208 (18) [M^+], 177 (22), 147 (68).

(12) **Preparation of β-Aryl-γ-butyrolactones 13 from Arenediazonium Tetrafluoroborates 2 and the THP Derivative of (*Z*)-2-Buten-1,4-diol (6) via a Sequential Palladium-Catalyzed Arylation–Cyclization–Oxidation Protocol – Typical Procedure**

To a stirred solution of **6** (128.2 mg, 0.50 mmol) and $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) in anhyd MeOH (4.0 mL), **2b** (250.0 mg, 1.0 mmol) was added at r.t. under argon. The reaction mixture was warmed at 35 °C and stirred for 45 min (the reactor was protected from light with aluminium film). After this time, the reaction mixture was diluted with Et_2O, washed with a sat. $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was filtrated through a short bed of SiO_2 and concentrated under reduced pressure. The crude was dissolved in CH_2Cl_2 (3 mL) and MCPBA (123.3 mg, 0.5 mmol; a commercially available 70% MCPBA was used) and $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol) were added. The cloudy reaction mixture was allowed to stir at r.t. for 24 h and then poured into an $NaHSO_3$ aq solution. The organic layer was removed, and the aqueous layer was washed with CH_2Cl_2. The organic layer was washed with aq $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel [*n*-hexane–EtOAc, 75:25 (v/v)] to afford 81.4 mg (74%) of **13b**.

Mp 78–80 °C. IR (KBr): 1778, 1714, 1282, 1012 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 8.3 Hz, 2 H), 4.68 (dd, J_1 = 8.8 Hz, J_2 = 7.9 Hz, 1 H), 4.28 (dd, J_1 = 8.9 Hz, J_2 = 7.9 Hz, 1 H), 3.90 (s, 3 H), 3.86 (qp, *J* = 8.3 Hz, 1 H), 2.96 (dd, J_1 = 9.1 Hz, J_2 = 8.8 Hz, 1 H), 2.68 (dd, J_1 = 8.8 Hz, J_2 = 17.2 Hz, 1 H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 175.9, 166.5, 144.7, 130.4, 129.7, 126.8, 73.6, 52.2, 41.0, 35.5. MS: *m/z* (%) = 220 (14) [M^+], 162 (59), 131 (100), 77 (89).